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54 **Process for the carbonylation of olefinically unsaturated compounds with a palladium catalyst.**

97 **Process for the carbonylation of olefins with CO**  
**in the presence of water, an alcohol and/or a carbox-**  
**ylic acid in the presence of a catalyst composition**  
**based on**

- a) a Pd compound,
- b) a protonic acid, and
- c) a phosphine  $PR^1R^2R^3$  in which  $R^1$  is a  
 heterocyclic ring having 5-6 atoms and containing 1  
 hetero N atom and  $R^2$  and  $R^3$  are  $R^1$  or an aryl  
 group.

**EP 0 282 142 A1**

# PROCESS FOR THE CARBONYLATION OF OLEFINICALLY UNSATURATED COMPOUNDS WITH A PALLADIUM CATALYST

The invention relates to a process for the carbonylation of an olefinically unsaturated compound with carbon monoxide in the presence of water, an alcohol and/or a carboxylic acid.

European patent specification No. 0 106 379 discloses a process in which an olefinically unsaturated compound is carbonylated with carbon monoxide in the presence of water, an alcohol and/or a carboxylic acid, a palladium catalyst, at least 5 mol of a phosphine  $PR^1R^2R^3$  in which  $R^1$ ,  $R^2$  and  $R^3$  each represent an optionally, substituted aryl group, per gram-atom of palladium, and, as promoter, an acid with a  $pK_a < 2$  (at 18 °C in aqueous solution), except hydrohalogenic and carboxylic acids.

Research carried out by the Applicant into these processes surprisingly has shown that the activity of the catalyst composition can be considerably enhanced whilst retaining a very high selectivity to carbonylated products, when an organic phosphine belonging to a special group is used. The selectivity to a certain compound, expressed in a percentage, is defined herein as  $100 \times a:b$  in which "a" is the amount of starting olefinically unsaturated compound that has been converted into that certain compound and "b" is the total amount of starting olefinically unsaturated compound that has been converted.

Accordingly, the present invention provides a process for the carbonylation of an olefinically unsaturated compound with carbon monoxide in the presence of water, an alcohol and/or a carboxylic acid, which process is carried out in the presence of a catalyst composition based upon

- a) a palladium compound,
- b) a protonic acid, and
- c) an organic phosphine of the general formula I



in which  $R^1$  represents a heterocyclic ring having 5 or 6 atoms in the ring which contains at least one hetero nitrogen atom in the ring and which may or may not be substituted and/or which may be part of a larger, condensed ring structure which may or may not be substituted and in which each of  $R^2$  and  $R^3$  has the same meaning as  $R^1$  or represents a substituted or unsubstituted aryl group.

The special group of organic phosphines mentioned hereinbefore is that of the general formula I.

The heterocyclic rings mentioned hereinbefore are preferably pyridyl, pyrazinyl, quinolyl, isoquinolyl, pyrimidinyl, pyridazinyl, indolizynyl, cinnolynyl, acridinyl, phenazinyl, phenanthridinyl, phenanthrolinyl, phthalazinyl, naphthyridinyl, quinoxalinyl or quinazolinyl groups. Among these groups pyridyl, pyrazinyl and pyridazinyl groups are preferred.

The heterocyclic rings and aryl groups mentioned hereinbefore may be substituted with one or more polar substituents or with one or more apolar substituents.

Examples of polar substituents which may be present are alkoxy groups, in particular those having not more than five carbon atoms and preferably methoxy and ethoxy groups; dimethylamino and diethylamino groups, in particular dimethylamino groups; chloro and fluoro atoms and trifluoromethyl, trichloromethyl and monochloromethyl groups. Examples of apolar substituents which may be present are alkyl groups having not more than five carbon atoms and preferably methyl and ethyl groups; other examples are n-propyl, 2-propyl and tert.-butyl groups.

The substituted or unsubstituted aryl groups represented by  $R^2$  and  $R^3$  in the general formula I suitably contain not more than 18 carbon atoms in the ring system and are preferably phenyl groups, but may be anthryl or naphthyl groups.

Phosphines of the general formula I in which  $R^1$  represents a pyridyl group,  $R^2$  a pyridyl or phenyl group and  $R^3$  a phenyl group are preferred.

According to a preferred embodiment of the present invention which not only allows very high selectivities to carbonylated products but also very high yields thereof, (2-pyridyl)diphenylphosphine is applied.

Other examples of suitable phosphines are:

di(p-methoxyphenyl)-2-pyridylphosphine  
 di(p-tolyl)-2-pyridylphosphine  
 di(o-methoxyphenyl)-2-pyridylphosphine  
 di(o-chlorophenyl)-2-pyridylphosphine  
 di(methoxyphenyl)-2-pyridylphosphine  
 di(m-chlorophenyl)-2-pyridylphosphine  
 di(p-methoxyphenyl)-3-pyridylphosphine  
 di(p-tolyl)-3-pyridylphosphine  
 di(o-methoxyphenyl)-3-pyridylphosphine  
 di(o-chlorophenyl)-3-pyridylphosphine  
 di(m-methoxyphenyl)-3-pyridylphosphine  
 di(m-chlorophenyl)-3-pyridylphosphine  
 di(p-methoxyphenyl)-4-pyridylphosphine  
 di(p-tolyl)-4-pyridylphosphine  
 di(o-methoxyphenyl)-4-pyridylphosphine  
 di(o-chlorophenyl)-4-pyridylphosphine  
 di(m-methoxyphenyl)-4-pyridylphosphine

di(m-chlorophenyl)-4-pyridylphosphine  
 diphenyl(3-methoxy-2-pyridyl)phosphine  
 diphenyl(4-methoxy-2-pyridyl)phosphine  
 diphenyl(4-chloro-2-pyridyl)phosphine  
 diphenyl(2-methoxy-3-pyridyl)phosphine  
 diphenyl(4-methoxy-3-pyridyl)phosphine  
 diphenyl(4-chloro-3-pyridyl)phosphine  
 diphenyl(3-methoxy-4-pyridyl)phosphine  
 diphenyl(3-chloro-4-pyridyl)phosphine  
 diphenyl(5-chloro-4-pyridyl)phosphine  
 diphenyl(5-methoxy-4-pyridyl)phosphine  
 di(p-tolyl)(3-methoxy-4-pyridyl)phosphine  
 di(p-tolyl)(3-chloro-4-pyridyl)phosphine  
 di(m-methoxyphenyl)(3-chloro-4-pyridyl)phosphine  
 di(m-methoxyphenyl)(3-methoxy-4-pyridyl)-  
 phosphine  
 di(m-chlorophenyl)(3-methoxy-4-pyridyl)phosphine  
 di(p-tolyl)(3-methoxy-2-pyridyl)phosphine  
 di(p-tolyl)(3-chloro-2-pyridyl)phosphine  
 di(m-methoxyphenyl)(3-chloro-2-pyridyl)phosphine  
 di(m-methoxyphenyl)(3-methoxy-2-pyridyl)-  
 phosphine  
 di(m-tert.butoxyphenyl)(3-chloro-2-pyridyl)-  
 phosphine  
 di(m-tert.butoxyphenyl)(3-methoxy-2-pyridyl)-  
 phosphine  
 di(m-tert.butoxyphenyl)(3-chloro-4-pyridyl)-  
 phosphine  
 di(m-tert.butoxyphenyl)(3-methoxy-4-pyridyl)-  
 phosphine  
 di(m-tert.butoxyphenyl)(2-methoxy-3-pyridyl)-  
 phosphine  
 di(m-tert.butoxyphenyl)(2-chloro-3-pyridyl)-  
 phosphine  
 di(m-chlorophenyl)(2-methoxy-3-pyridyl)phosphine  
 di(m-chlorophenyl)(2-chloro-3-pyridyl)phosphine  
 di(o-chlorophenyl)(2-methoxy-3-pyridyl)phosphine  
 di(p-methoxyphenyl)-2-pyrimidinylphosphine  
 di(p-tolyl)-2-pyrimidinylphosphine  
 di(o-methoxyphenyl)-2-pyrimidinylphosphine  
 di(o-chlorophenyl)-2-pyrimidinylphosphine  
 di(m-methoxyphenyl)-2-pyrimidinylphosphine  
 di(p-methoxyphenyl)-2-pyridazinylphosphine  
 di(p-tolyl)-2-pyridazinylphosphine  
 di(o-methoxyphenyl)-2-pyridazinylphosphine  
 di(o-chlorophenyl)-2-pyridazinylphosphine  
 di(m-methoxyphenyl)-2-pyridazinylphosphine  
 di(p-methoxyphenyl)(3-methoxy-2-pyrimidinyl)-  
 phosphine  
 di(p-tolyl)(3-methoxy-2-pyridinyl)phosphine  
 di(o-chlorophenyl)(3-chloro-2-pyrimidinyl)phosphine  
 di(m-methoxyphenyl)(3-chloro-2-pyrimidinyl)-  
 phosphine  
 di(p-tolyl)(4-methoxy-3-pyridazinyl)phosphine  
 di(p-methoxyphenyl)(4-methoxy-3-pyridazinyl)-  
 phosphine  
 di(o-chlorophenyl)(4-methoxy-3-pyridazinyl)-  
 phosphine

phenyl-di(3-methoxy-2-pyridyl)phosphine  
 phenyl-di(4-methoxy-2-pyridyl)phosphine  
 phenyl-di(4-chloro-2-pyridyl)phosphine  
 phenyl-di(2-methoxy-3-pyridyl)phosphine  
 phenyl-di(4-methoxy-3-pyridyl)phosphine  
 phenyl-di(4-chloro-3-pyridyl)phosphine  
 phenyl-di(3-methoxy-4-pyridyl)phosphine  
 phenyl-di(3-chloro-4-pyridyl)phosphine  
 phenyl-di(5-chloro-4-pyridyl)phosphine  
 phenyl-di(5-methoxy-4-pyridyl)phosphine  
 phenyl-di(3-methoxy-2-pyrimidinyl)phosphine  
 phenyl-di(3-chloro-2-pyrimidinyl)phosphine  
 phenyl-di(4-methoxy-2-pyrimidinyl)phosphine  
 phenyl-di(4-methoxy-3-pyridazinyl)phosphine and  
 phenyl-di(4-chloro-3-pyridazinyl)phosphine.

As protonic acids a large variety of acids or  
 mixture of acids may be applied. Examples of such  
 acids are orthophosphoric acid, pyrophosphoric  
 acid, sulphuric acid, hydrohalogenic acids, benzene  
 phosphonic acid, benzenesulphonic acid, p-  
 toluenesulphonic acid, naphthalenesulphonic acid,  
 toluenephosphonic acid, chlorosulphonic acid,  
 fluorosulphonic acid, monochloroacetic acid, dich-  
 loraacetic acid, trichloroacetic acid, trifluoroacetic  
 acid, oxalic acid, terephthalic acid, perchloric acid,  
 2-hydroxypropane-2-sulphonic acid,  
 trifluoromethanesulphonic acid and mixtures there-  
 of. Among these acids p-toluenesulphonic acid and  
 benzenephosphonic acid are preferred.

Where a non-carboxylic acid having a pKa  
 greater than 2, measured at 18 °C in aqueous  
 solution, and/or a sterically hindered carboxylic  
 acid having a pKa below 4.5, also measured at 18  
 °C in aqueous solution, is applied, preferably at  
 least 1 mol of such acids is used per mol of  
 organic phosphine of the general formula I. Exam-  
 ples of preferred non-carboxylic acids having a pKa  
 greater than 2 are benzenephosphonic acid and  
 orthophosphoric acid. Arsenic acid is another ex-  
 ample of such acids. The carboxylic acid being  
 sterically hindered means that atoms or groups of  
 atoms are present which interfere with one another,  
 thus counteracting esterification of the acid. Exam-  
 ples of such acids are 2,6-dimethylbenzoic acid  
 and 2,6-diethylbenzoic acid. It is preferred to apply  
 sterically hindered carboxylic acids having a pKa  
 below 2. Among the sterically hindered carboxylic  
 acids preference is given to the sterically hindered  
 benzoic acids, for example 2,6-dichlorobenzoic  
 acid, 2,6-difluorobenzoic acid, 2,4,6-trifluorobenzoic  
 acid, 2,4,6-trichlorobenzoic acid, 2,6-dibromoben-  
 zoic acid, 2,4,6-tribromobenzoic acid, 2,6-di-  
 iodobenzoic acid and 2,4,6-triiodobenzoic acid.

Hydrohalogenic acid may in principle, be used  
 but they have the known disadvantage that they  
 may cause a corrosive effect.

Both homogeneous and heterogeneous pal-  
 ladium compounds may be used in the process

according to the present invention. Homogeneous compounds are preferred. Suitable homogeneous compounds are palladium salts of nitric acid, sulphuric acid and alkanolic acids having not more than 12 carbon atoms per molecule.

Salts of hydrohalogenic acids may, in principle, be used as well, but they have the drawback that the halogen ion may have a corrosive effect.

A palladium compound used by preference is palladium acetate. Moreover, palladium complexes may be used, for instance palladium acetylacetonate, tetrakis(triphenylphosphine)palladium, bis(tri-*o*-tolylphosphine)palladium acetate, bis(triphenylphosphine)palladium sulphate, bis(diphenyl-2-pyridylphosphine)palladium acetate, tetrakis(diphenyl-2-pyridylphosphine) palladium, bis(di-*o*-tolylpyridyl)phosphinepalladium acetate and bis(diphenylpyridyl)phosphine palladium sulphate. Palladium on charcoal and palladium bonded to an ion exchanger - for instance an ion exchanger comprising sulphononic acid groups - are examples of suitable heterogeneous catalysts.

The quantity of catalyst composition used in the present process may vary within wide ranges. Preferably, per mol of olefinically unsaturated compound to be carbonylated, such a quantity of catalyst is used as to contain in the range of from  $10^{-7}$  to  $10^{-1}$  and in particular from  $10^{-6}$  to  $10^{-3}$  gram-atom of palladium.

The organic phosphine may be used in an amount per gram-atom palladium which is not critical and may vary within wide ranges. Preferably, this amount is in the range of from 2 to 500 mol per gram-atom palladium. In general, amounts of more than 1000 mol organic phosphine per gram-atom of palladium are not necessary.

The protonic acid may be used in an amount per equivalent of organic phosphine which is not critical and may vary within wide ranges. Preferably, this amount is in the range of from 0.1 to 50 equivalents per equivalent of organic phosphine.

It has, furthermore, been found that the reaction rate in the process according to the present invention can be maintained very high by the application of a catalyst stabilizer in catalytic amounts. Examples of such stabilizers are mentioned in Netherlands patent application No. 8603302, filed 24th December, 1986, which application is incorporated herein by reference. N-methylpyrrolidone is an attractive example of such a catalyst stabilizer.

It is not necessary to carry out the process according to the present invention in the presence of a separate solvent, a large excess of one of the reactants, usually the alcohol, often forming a suitable liquid phase. If required, however, a separate solvent may be used. Any inert solvent may be used for this purpose. Examples of suitable sol-

vents are dimethyl sulphoxide, diisopropyl sulphone, tetrahydrothiophene 1,1-dioxide (also referred to as a "sulfolane"), 2-methylsulfolane, 3-methylsulfolane, 2-methyl-4-butylsulfolane; aromatic hydrocarbons such as benzene, toluene and the three xylenes; esters such as methyl acetate and gamma-butyrolactone; ketones such as acetone and methyl isobutyl ketone; ethers such as anisole, 2,5,8-trioxanonane (also referred to as "diglyme"), diphenyl ether and diisopropyl ether.

The carbonylation according to the invention is preferably carried out at a temperature in the range of from 20 to 200 °C, in particular from 50 to 150 °C. The overall pressure preferably lies between 1 and 100, in particular 5 and 75 bar.

The molar ratio of the olefinically unsaturated compound to water, alcohol or carboxylic acid is not critical. The molar ratio between hydroxy groups and olefinic double bonds may lie for instance between 0.01:1 and 100:1, and will usually be between 0.1:1 and 10:1. When using a mono-olefin and either water, a monohydric alcohol or a monobasic acid, preference is usually given to the use of an excess of the hydroxy compound mentioned. However, when using a polyhydric alcohol or a polybasic acid to prepare a polyester or a polyanhydride, it will generally be necessary to use an excess of olefinic compound.

The olefinically unsaturated compound may be an unsubstituted or a substituted alkene or cycloalkene preferably having 2-30, and in particular 2-20, carbon atoms per molecule and preferably 1-3 carbon-carbon double bonds per molecule. The alkene or cycloalkene may be substituted, for instance, with one or more halogen atoms or cyano, ester, alkoxy, hydroxy, carboxy or aryl groups. If the substituents are not inert under the reaction conditions, the carbonylation reaction may be accompanied with other reactions. For instance, the carbonylation of allyl alcohol is accompanied with esterification of the hydroxy group. Examples of suitable olefinic compounds are ethene, propene, 1-butene, 2-butene, isobutene, the isomeric pentenes, hexenes, octenes and dodecenes, 1,5-cyclooctadiene, cyclododecene, 1,5,9-cyclododecatriene, allyl alcohol, methyl acrylate, ethyl acrylate, methyl methacrylate, acrylonitrile, acrylamide, N,N-dimethylacrylamide, vinyl chloride, allyl chloride, acrolein, oleic acid, methyl allyl ether and styrene. Very good results have been obtained with ethylene.

The alcohols or carboxylic acids used in the process according to the invention may be aliphatic, cycloaliphatic or aromatic and may be substituted with one or more substituents, such as mentioned hereinbefore in connection with the olefinically unsaturated compounds to be used as starting material. The alcohol may therefore also be

a phenol. The alcohols or carboxylic acids preferably contain not more than 20 carbon atoms per molecule. Examples of suitable alcohols are methanol, ethanol, propanol, isobutanol, tert.butanol, stearyl alcohol, benzyl alcohol, cyclohexanol, allyl alcohol, a chlorocapryl alcohol, ethylene glycol, 1,2-propanediol, 1,4-butanediol, glycerol, polyethylene glycol, 1,6-hexanediol, phenol and cresol. Examples of suitable carboxylic acids are formic acid, acetic acid, propionic acid, butyric acid, caproic acid, trimethylacetic acid, benzoic acid, caprylic acid, succinic acid, adipic acid and hydroxycaproic acid. Special preference is given to alkanols and carboxylic acids having 1-10 carbon atoms per molecule. If the alcohol or the carboxylic acid has more than one hydroxy group or carboxy group, different products may be formed, depending on the molar ratios existing between the reagents. For instance, depending on the quantity of olefinically unsaturated compound used, either a mono-ester or a diester may be produced from glycerol. Another example of a polyvalent alcohol is a sugar.

The products formed in the process according to the invention may be further reacted if desired. For instance, the carbonylation of an olefin, when conducted in the presence of water, yields a carboxylic acid which, by reaction with a further quantity of olefin, may form a carboxylic anhydride. When the carbonylation is carried out in the presence of an alcohol, it yields an ester which, when water is present as well, may hydrolyze to form an acid and an alcohol, each of which may again react with an olefin. When the carbonylation is carried out in the presence of a carboxylic acid, it yields a carboxylic anhydride which, when water is present as well, may hydrolyze to form one or more carboxylic acids which in their turn may react with a further quantity of olefin.

Reaction of an alkanecarboxylic acid having  $n+1$  carbon atoms with an olefin having  $n$  carbon atoms yields the symmetrical anhydride of the alkanecarboxylic acid having  $n+1$  carbon atoms. This anhydride may optionally be hydrolyzed, half of the carboxylic acid formed may be collected as a product and the other half recycled to the carbonylation reactor. The process thus leads to the conversion of an olefin having  $n$  carbon atoms into a carboxylic acid having  $n+1$  carbon atoms.

In the process according to the invention the carbon monoxide may be used pure or diluted with an inert gas, such as nitrogen, noble gases or carbon dioxide. Generally the presence of more than 10 %v of hydrogen is undesirable, since under the reaction conditions it may cause hydrogenation of the olefinic compound. Generally preference is given to the use of carbon monoxide or a carbon monoxide-containing gas which contains less than 5 %v of hydrogen. Suitably, a molar ratio

carbon monoxide to olefinically unsaturated compound in the range of from 0.1:1 to 10:1 is used.

During the process according to the present invention one or more of the three components of the catalyst composition may be supplied, continuously or intermittently, to compensate for possible losses thereof, if any such losses might occur.

The following Examples further illustrate the invention.

#### Example 1

Propionic anhydride was prepared as follows. A magnetically stirred Hastelloy C autoclave ("Hastelloy" is a trade mark) of 250 ml capacity was charged with a catalyst solution comprising 50 ml of propionic anhydride, 10 ml of propionic acid, 0.1 mmol of palladium acetate, 3 mmol of p-toluenesulphonic acid, and 5 mmol of (2-pyridyl)diphenylphosphine.

After any air present in the autoclave had been removed by evacuation, ethene was introduced with pressure until a pressure of 20 bar was reached, followed by carbon monoxide until a pressure of 50 bar was reached. Subsequently, the contents of the autoclave were heated to 105 °C. After 1 h the carbonylation was terminated by cooling to room temperature and then releasing the pressure. Analysis of the contents of the autoclave by means of gas-liquid chromatography showed that propionic anhydride had been formed with a rate of 1340 mol per mol palladium per hour and that the conversion of propionic acid was 76%.

#### Comparative Experiment A

Example 1 was repeated with the differences that triphenylphosphine (5 mmol) instead of (2-pyridyl)diphenylphosphine (5 mmol) and a temperature of 130 °C instead of 105 °C were used. Propionic anhydride had been formed with a rate of 380 mol per mol palladium per hour and the conversion of propionic acid was 24%.

Comparison of Example 1 carried out at 105 °C and using a catalyst composition which contained a phosphorus/nitrogen compound as the component c) with Comparative Experiment A carried out at 130 °C and using a catalyst composition which contained a triarylphosphine as the component c) shows that when the process according to the present invention is carried out a higher reaction rate can be achieved at lower temperatures.

### Example 2

Example 1 was repeated with the difference that N-methylpyrrolidone (58 mmol) was also present. Propionic anhydride has been formed with a rate of 1375 mol per mol palladium per hour and the conversion of propionic acid was 88%.

Comparison of Example 1 carried out in the absence of a stabilizer with Example 2 carried out in the presence of N-methylpyrrolidone as a stabilizer shows that the presence of a stabilizer allows a higher reaction rate.

### Example 3

Phenyl propionate was prepared in substantially the same way as propionic anhydride in Example 1, the differences being:

- a) the catalyst solution contained  
40 ml of dimethyl carbonate,  
10 g of phenol,  
0.1 mmol of palladium acetate,  
2 mmol of p-toluenesulphonic acid,  
3 mmol of (2-pyridyl)diphenylphosphine, and
- b) the reaction temperature was 120 °C.

The reaction rate was 150 g phenyl propionate per g palladium per hour and the selectivity to phenyl propionate was 95%.

### Comparative Experiment B

Example 3 was repeated with the difference that triphenylphosphine (3 mmol) instead of (2-pyridyl)diphenylphosphine (3 mmol) was used. The reaction rate was 75 g phenyl propionate per g palladium per hour.

Comparison of Example 3 carried out using a catalyst composition which contained a phosphorus/nitrogen compound as the component c) with Comparative Experiment B using a catalyst composition which contained a triarylphosphine as the component c) shows that when the process according to the present invention is carried out a higher reaction rate can be achieved.

### Example 4

Propionic acid was prepared in substantially the same way as propionic anhydride in Example 1, the differences being:

- a) the catalyst solution contained  
40 ml of diglyme  
10 ml of water,

- 0.1 mmol of palladium acetate,  
2 mmol of p-toluenesulphonic acid, and  
3 mmol of (2-pyridyl)diphenylphosphine, and
- b) the reaction temperature was 100 °C instead of 105 °C.

Propionic acid had been formed with a rate of 1400 g per g palladium per h and the selectivity to this acid was more than 95%.

### Example 5

Propionic anhydride was prepared in substantially the same way as in Example 1, the differences being:

- a) the catalyst solution contained  
50 ml of anisole,  
10 ml of propionic acid,  
0.1 mmol of palladium acetate,  
2 mmol of p-toluenesulphonic acid, and  
3 mmol of (2-pyridyl)diphenylphosphine, and
- b) the reaction temperature was 90 °C, the partial pressures of ethylene and carbon monoxide were 30 bar each and the reaction time was 3 hours.

Propionic anhydride had been formed with a rate of 1500 g per g palladium per hour and with a selectivity of more than 95%.

### Example 6

Propionic anhydride was prepared in substantially the same way as in Example 1, the differences being:

- a) the catalyst solution contained  
50 ml of propionic anhydride,  
10 ml of propionic acid,  
0.05 mmol of palladium acetate,  
1.5 mmol of p-toluenesulphonic acid, and  
2.5 mmol of di(2-pyridyl)phenylphosphine, and
- b) the reaction temperature was 120 °C instead of 105 °C.

Propionic anhydride had been formed with a rate of 890 mol per gram-atom palladium per hour and the conversion of propionic acid was 37%.

### Example 7

Ethylene was carbonylated in substantially the same way as in Example 1, the differences being:

- a) the catalyst solution contained  
40 ml of anisole,  
20 ml of acetic acid,  
0.1 mmol of palladium acetate,  
2 mmol of p-toluenesulphonic acid, and  
3 mmol of (2-pyridyl)diphenylphosphine, and

b) the reaction temperature was 90 °C instead of 105 °C and the reaction time was 5 hours instead of 1 hour.

Carbonylation products had been formed with a rate of 500 mol per gram-atom palladium per hour and these products consisted of 80 mmol of acetic propionic anhydride, 120 mmol of acetic anhydride, 110 mmol of propionic acid and about 10 mmol of propionic anhydride.

#### Example 8

Ethylene was carbonylated in substantially the same way as in Example 7, the differences being that 30 ml of methanol and 10 ml of propionic acid were present instead of 20 ml of acetic acid and that the reaction temperature was 95 °C instead of 90 °C.

Methyl propionate had been formed with a rate of 1000 mol per gram-atom palladium per hour.

#### Claims

1. A process for the carbonylation of an olefinically unsaturated compound with carbon monoxide in the presence of water, an alcohol and/or a carboxylic acid, which process is carried out in the presence of a catalyst composition based upon

- a) a palladium compound,
- b) a protonic acid, and
- c) an organic phosphine of the general formula I



in which R<sup>1</sup> represents a heterocyclic ring having 5 or 6 atoms in the ring which contains at least one hetero nitrogen atom in the ring and which may or may not be substituted and/or which may be part of a larger, condensed ring structure which may or may not be substituted and in which each of R<sup>2</sup> and R<sup>3</sup> has the same meaning as R<sup>1</sup> or represents a substituted or unsubstituted aryl group.

2. A process as claimed in claim 1 in which said heterocyclic rings are pyridyl, pyrazinyl, quinolyl, isoquinolyl, pyrimidinyl, pyridazinyl, indolizynyl, cinnolynyl, acridinyl, phenazinyl, phenanthridinyl, phenanthrolinyl, phthalazinyl, naphthyridinyl, quinoxalinyl or quinazolinyl groups.

3. A process as claimed in claim 1 in which said heterocyclic rings are pyridyl, pyrazinyl or pyridazinyl groups.

4. A process as claimed in any one of the preceding claims in which R<sup>2</sup> and R<sup>3</sup> each represent a phenyl group.

5. A process as claimed in any one of the preceding claims in which the heterocyclic rings and aryl groups are substituted with one or more polar substituents.

6. A process as claimed in claim 5 in which the polar substituents are alkoxy groups having not more than five carbon atoms, chloro or fluoro atoms, trifluoromethyl, trichloromethyl, monochloromethyl and/or diethylamino groups.

7. A process as claimed in claim 5 in which the substituents are methoxy, ethoxy, methyl, ethyl or dimethylamino groups.

8. A process as claimed in any one of claims 1 to 4 in which the heterocyclic rings and aryl groups are substituted with one or more apolar groups.

9. A process as claimed in claim 8 in which the substituents are alkyl groups having not more than five carbon atoms.

10. A process as claimed in claim 1 in which a phosphine of the general formula I is applied in which R<sup>1</sup> represents pyridyl, R<sup>2</sup> pyridyl or phenyl and R<sup>3</sup> phenyl.

11. A process as claimed in any one of the preceding claims in which as protonic acid p-toluenesulphonic acid or benzenephosphonic acid is used.

12. A process as claimed in any one of the preceding claims in which as palladium compound palladium acetate is applied.

13. A process as claimed in any one of the preceding claims in which the palladium compound is used in an amount in the range of from 10<sup>-7</sup> to 10<sup>-1</sup> gram-atom palladium per mol olefinically unsaturated compound.

14. A process as claimed in any one of the preceding claims in which the organic phosphine is used in an amount in the range of from 2 to 500 mol per gram-atom palladium.

15. A process as claimed in any one of the preceding claims in which the protonic acid is used in an amount in the range of from 0.1 to 50 equivalents per equivalent of organic phosphine.

16. A process as claimed in any one of the preceding claims which is carried out in the presence of a catalyst stabilizer.

17. A process as claimed in any one of the preceding claims in which an amount of water, alcohol and/or carboxylic acid in the range of from 0.01 to 100 mol per mol of olefinically unsaturated compound is used.

18. A process as claimed in any one of the preceding claims which is carried out at a pressure in the range of from 1 to 100 bar and a temperature in the range of from 20 °C to 200 °C.

19. A process as claimed in any one of the preceding claims in which an unsubstituted or a substituted alkene or cycloalkene having in the range of from 2 to 30 carbon atoms per molecule is carbonylated.

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European Patent  
Office

# EUROPEAN SEARCH REPORT

Application number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 88200462.5
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	DE - A - 2 410 246 (SHELL) * Claims *	1,13, 17-19	C 07 C 53/122 C 07 C 51/14
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A	GB - A - 998 974 (UNILEVER) * Claims; example 6 *	1,11	
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			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 07 C 51/00 C 07 C 53/00
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 05-05-1988	Examiner HOFBAUER
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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